Measurement of the Relaxation Rate of the Magnetization in $Mn_{12}O_{12}$-Acetate Using Proton NMR Echo

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We present a novel method to measure the relaxation rate W of the magnetization of $Mn_{12}O_{12}$-acetate (Mn12) magnetic molecular cluster in its $S = 10$ ground state at low T. It is based on the observation of an exponential growth in time of the proton NMR signal during the thermal equilibration of the magnetization of the molecules. We can explain the novel effect with a simple model which relates the intensity of the proton echo signal to the microscopic reversal of the magnetization of each individual Mn12 molecule during the equilibration process. The method should find wide application in the study of magnetic molecular clusters in off-equilibrium conditions.

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Recently the successes in synthesizing identical magnetic molecules forming solid crystal lattices has given a new impulse to the study of mesoscopic magnetism [1]. Among the molecules is $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (in short Mn12) [2,3] which has attracted much recent interest since the study of the relaxation of the macroscopic magnetization at low temperature has revealed deviations from classical superparamagnetic behavior [4,5], pronounced peaks of the relaxation rate as a function of applied magnetic field [6–8], and quantum steps in the hysteresis loop [9–11]. Mn12 in its magnetic ground state has a total high spin $S = 10$ with splitting of the magnetic m sublevels by a large easy-axis anisotropy. An important issue regards the mechanism responsible for the reversal of the magnetization of the molecule at low T against the anisotropy barrier ($\approx$60 K). The peaks of the relaxation rate vs applied magnetic field and the quantum steps in the hysteresis loop occur when spin states become pairwise degenerate suggesting that resonant tunneling of the magnetization plays a role. The theoretical explanation of the experimental observations involves both thermal excitations and quantum resonant tunneling transitions [12–20].

In this Letter we present a novel method to measure the relaxation of the macroscopic magnetization based on a nuclear magnetic resonance (NMR) experiment. The method is based on the observation that the proton NMR echo intensity changes in time when the measurement is done off equilibrium, i.e., during the recovery of the Mn12 magnetization toward equilibrium. It is found that the time dependence of the NMR echo intensity is governed by an exponential law whose time constant yields directly the relaxation time of the Mn12 magnetization. We account for this effect by considering the change of the local field at the nuclear site due to the reversal of the magnetization of individual molecules. Since the number of nuclei affected by the change of local field is different when the reversal of the magnetization occurs via direct tunneling with respect to multiple thermal excitations over the barrier we conjecture that the present experiment contains in principle information about the paths followed by the Mn12 molecular magnetization in the process of relaxation.

Proton pulse NMR experiments were performed with a Midcontinent NMR pulse Fourier transform (FT) spectrometer. The echo is generated with a $\pi/2$-π pulse sequence at the resonance frequency corresponding to the center of the weakly shifted peak in the spectrum [21] and the echo intensity was monitored as a function of time. Typical $\pi/2$ pulse length was 3.5–4.5 μs and delay τ between $\pi/2$ pulse and π pulse was in most cases 50 μs. Polycrystalline samples of Mn12 were prepared as described in Ref. [3]. The powder sample was aligned with the anisotropy axis along the magnetic field by letting the sample sit at 4.2 K in a field of $\sim$1.8 T for several hours. This procedure should lead to an alignment of about 80%. Then the field was turned off and the system was left in zero field to reach thermal equilibrium (zero average magnetization) for about 2–3 hours. The temperature was then lowered slowly and the field was turned on in less than 2 min. The subsequent increase of the echo intensity with time was monitored continuously by averaging over 3, 7.5, 15 min time slots depending on the relaxation time. A typical recovery curve is shown in Fig. 1. All experimental curves could be fitted very well with the equation

$$h(t) = a(1 - e^{-Wt}) + b = (a + b)\left(1 - \frac{a}{a + b} e^{-Wt}\right), \qquad (1)$$

where W is the rate of growth of the echo intensity, $(a + b)$ is the equilibrium intensity of echo signal, i.e., $h(\infty)$, and $a/(a + b)$ is the initial fractional reduction of the echo intensity. The origin in time is taken at the moment when the magnetic field is turned on.

We made careful checks which could rule out the possibility that the observed changes of echo with time is due to

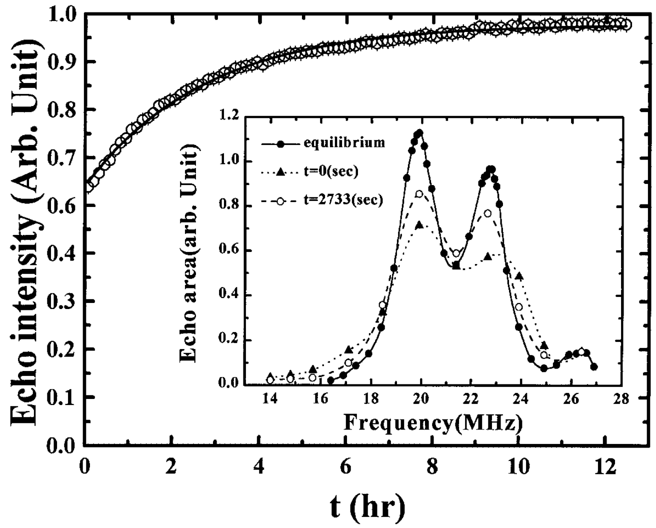

FIG. 1. Echo intensity plotted as a function of the time elapsed after turning on the magnetic field at $T = 2.5$ K and $H = 0.5$ T. The full line is a best fit according to Eq. (1). The echo intensity was measured with the irradiation frequency close to the lower frequency peak in the spectrum (see inset) which almost coincides with the Larmor frequency. Inset: time evolution of NMR spectrum at 2.5 K and 0.46 T (proton Larmor frequency = 19.9 MHz.

instrumental effects (changes in resonance frequency of the coil, changes in Q factor of the coil, changes in amplification parameters of the receiver). To rule out the presence of narrowing effects we measured the proton NMR spectrum in equilibrium and off equilibrium by plotting the area under the echo signal as a function of measuring frequency after correcting for changes of sensitivity of the spectrometer as a function of frequency (see the inset in Fig. 1). As one can see there is only a slight change in the width of the spectrum which falls into the uncertainty of the normalization correction. We conclude that the observed time dependence of the echo measured at the frequency of the lower frequency peak appears to be an intensity change of the signal at constant width of the spectrum. Finally it is noted that the equilibrium proton spin-lattice relaxation time is about 6 orders of magnitude shorter [21] than the time scale over which the echo intensity changes and thus should play no role here.

In a Hahn echo experiment one probes the irreversible dephasing of the transverse nuclear magnetization during the time interval τ between the two radio frequency pulses [22]. If some nuclei are subjected to a change of average local field between the time window τ, separating the $\pi/2$ pulse from the π pulse and the second one separating the π pulse from the echo signal, then those nuclei will not refocus at time 2τ and will not contribute to the echo intensity. This circumstance has been used extensively, e.g., to measure diffusion in a magnetic field gradient [23] or more recently to study flux lines motion in superconductors [24]. In the present case the reduction of the echo intensity is ascribed to the changes of average local hyperfine field resulting from changes of average orientation of the Mn moments which are maximum at off equilibrium and decrease to zero as the final thermal equilibrium is reached. A possible effect on the dephasing of the proton echo due to the interaction with the ^{57}Mn nuclei (similar to what is observed in superconductors [25]) cannot be easily explored for lack of information on the ^{57}Mn NMR.

We now describe a simple model which accounts for the experimental observations and which defines the physical meaning of the parameters in Eq. (1). If we assume that the reduction of echo height is proportional to the number of spins which are influenced by the local field change we can express the echo height as

$$h(t) \propto [N_p N_m - N_p^{\mathrm{ch}}(t)], \tag{2}$$

where N_p is the number of protons in a single Mn12 molecule, N_m is total number of molecules, and $N_p^{\mathrm{ch}}(t)$ is the number of protons which undergo a change of average local field between the time interval separating the $\pi/2$-π pulses and the one separating the π pulse and the echo. At low temperature Mn12 occupies a magnetic ground state with total spin $S = 10$ [3] split in zero field into 11 levels by crystal field anisotropy. When the external magnetic field is applied along the easy axis as in our case the system relaxes towards the magnetized state by a net flow of magnetization from one to the other of the two $m = \pm 10$ states with a redistribution of the population in the intermediate excited states. We will make the simplifying assumption that during the relaxation process the ratio of the population between adjacent intermediate states is described by Boltzmann statistics with a single spin temperature different from lattice temperature [26]. The common spin temperature should be easily maintained by the dipolar intermolecular interactions. Then we can use a two level system master equation:

$$\begin{aligned} \frac{dN_+}{dt} &= -W_+N_+ + W_-N_- , \\ \frac{dN_-}{dt} &= -W_-N_- + W_+N_+ , \end{aligned} \tag{3}$$

where W_- is the average transition rate from $m = -10$ to $m = +10$, and W_+ from $m = +10$ to $m = -10$ and both transition rates depend on barrier height and are assumed to be time independent. By solving these master equations we get the number of transitions from $m = +10$ to $m = -10$ and vice versa per unit time interval around t. We can express these two quantities as magnetization currents: $J_+(t) \equiv W_+N_+(t)$ and $J_-(t) \equiv W_-N_-(t)$, respectively. The general expressions of the magnetization currents with initial conditions $N_+(t = 0) = N_-(t = 0) = N_m/2$ can be found easily. For the present purpose, it is sufficient to give the approximate solution obtained under the approximation $W_- \gg W_+$. In fact, the ratio W_+/W_- is less than 0.05 below 2.4 K with field larger than 0.25 T. Setting $W_- = W$, one has

$$J_+(t) \cong 0 \quad \text{and} \quad J_-(t) \cong N_m/2\ W \exp(-Wt). \tag{4}$$

Since $W\tau$ is very small ($\sim 10^{-11}$), a small fraction of molecules change their orientation in the time interval τ. Consequently, the probability for a given proton to experience local field changes due to Mn12 spin flip in both first and second time interval τ is negligible. Thus, for the purpose of evaluating $N_p^{\mathrm{ch}}(t)$ in Eq. (2), we can calculate the number of spin flip in either interval independently and add them together. Then the expression for the fraction of total molecules, $P_m^{\mathrm{flip}}(t)$, which change orientation in the time intervals τ is

$$P_m^{\mathrm{flip}}(t) = \frac{1}{N_m}\left[\int_t^{t+\tau} J_-(t)\,dt + \int_{t+\tau}^{t+2\tau} J_-(t)\,dt\right] = \frac{1}{2}(1 - e^{-2W\tau})e^{-W(t+2\tau)}. \tag{5}$$

We define N_m^{eff} as the effective number of molecules whose protons are affected by the local field change due to a molecular spin flip. Then Eq. (2) can be rewritten as

$$h(t) = h_0 \exp\left(-\frac{2\tau}{T_2}\right)[1 - N_m^{\mathrm{eff}} P_m^{\mathrm{flip}}(t)] \cong h_0 \exp\left(-\frac{2\tau}{T_2}\right)[1 - N_m^{\mathrm{eff}} W\tau e^{-Wt}], \tag{6}$$

where $P_m^{\mathrm{flip}}(t)$ is given by Eq. (5), $h_0 \exp(-2\tau/T_2)$ is the echo amplitude at equilibrium ($t \Rightarrow \infty$) with the effect of the nuclear spin-spin relaxation time T_2 included. In obtaining Eq. (6), we have assumed $t \gg \tau$ and $W\tau \ll 1$ since $\tau = 50\ \mu$s and W is small at low temperatures. By comparing Eqs. (1) and (6), we see that our simple model predicts that the rate of growth of the echo intensity vs time is indeed the relaxation rate of the Mn12 magnetization. Our values of relaxation time $\tau_r (= 1/W)$ derived from Eq. (1) as a function of temperature at 0.45 T are compared in Fig. 2 with the results obtained in Mn12 from magnetization [6] and specific heat [27] measurements. The NMR set of data shows little scatter and is in good agreement with the measurements obtained at approximately the same field H with the SQUID, confirming that we have a new microscopic method to study the relaxation of magnetization in molecular clusters. Measurements of τ_r were also performed as a function of applied magnetic field at $T = 2.4$ K. The results are shown in Fig. 3. The behavior is consistent with the previously reported magnetization results which indicated minima in the relaxation time at field values corresponding to magnetic level crossings [6]. The background relaxation due to thermal excitations over the barrier is well represented by an exponential law: $\tau_r = \tau_0 \exp[(D - g\mu_B \vec{S} \cdot \vec{H})/k_B T]$ with $g = 2$, $S = 10$, $\tau_0 \cong 8.10^{-7}$, zero-field barrier height $D = 66$ K (see full line in Fig. 3).

We turn now to the interpretation of the constants a, b in Eq. (1). From the comparison of Eqs. (1) and (6) we find that the fractional echo amplitude change is $a/(a + b) = N_m^{\mathrm{eff}} W\tau$, where $W\tau$ is the average fractional number of molecules which have flipped completely in time τ and N_m^{eff} is the effective number of molecules whose protons are affected by the local field change due to a molecular spin flip. As shown in Fig. 4 the fractional echo amplitude change has large fluctuations around a constant value independent of $W\tau$ implying that N_m^{eff} is itself inversely proportional to $W\tau$. This can be understood as a saturation effect. In fact, as $W\tau$ (i.e., the number of molecules flipping in the time interval τ) increases, adjacent flipping molecules superimpose their effect on the same protons in nearby molecules and the net effect is thus reduced. Next we give an estimate of nonsaturated value of N_m^{eff}, i.e., N_m^0. We use the criterion that the local field change at the proton site should be at least the same as the proton

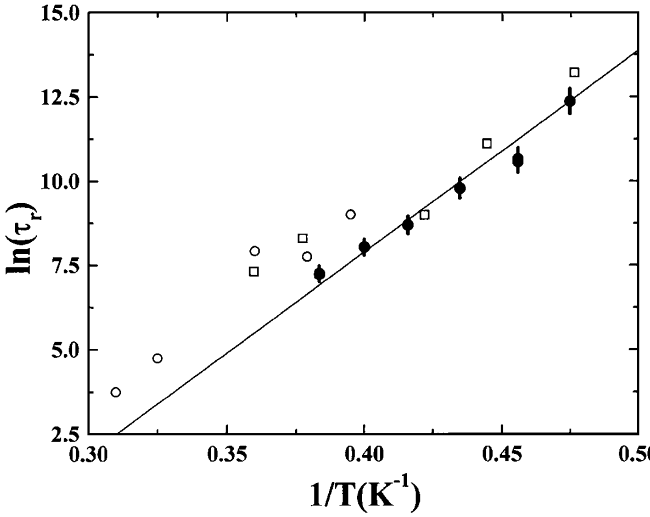

FIG. 2. Semilog plot of the relaxation time of the magnetization of Mn12 at $H = 0.45$ T vs the inverse of the temperature. (●) ^{1}H NMR echo height evolution at $H = 0.45$ T; (□) SQUID measurements at $H = 0.44$ T [6]; (○) specific heat measurements at $H = 0$ [26]. The full line corresponds to the Arrhenius law $\tau_r = 10^{-7} \exp(60/T)$.

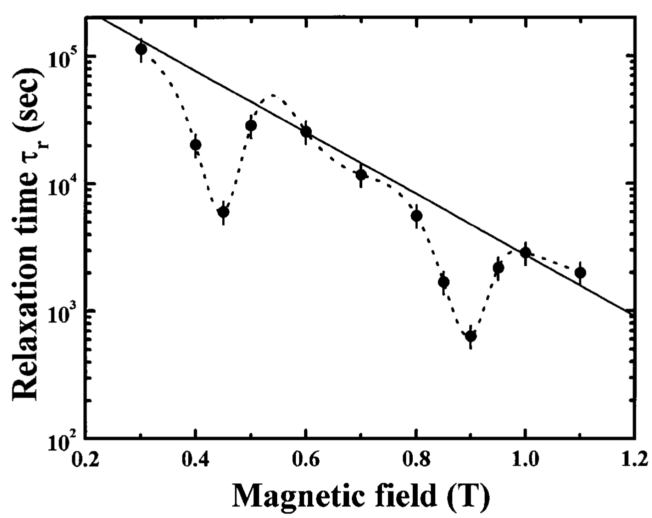

FIG. 3. Relaxation time of the magnetization of Mn12 vs magnetic field at 2.4 K measured from the NMR echo. The solid line corresponds to the Arrhenius law $\tau_r = 7 \times 10^5 \exp(-13.3H/2.4)$ with H in tesla (see text). The dotted line is a spline fit.

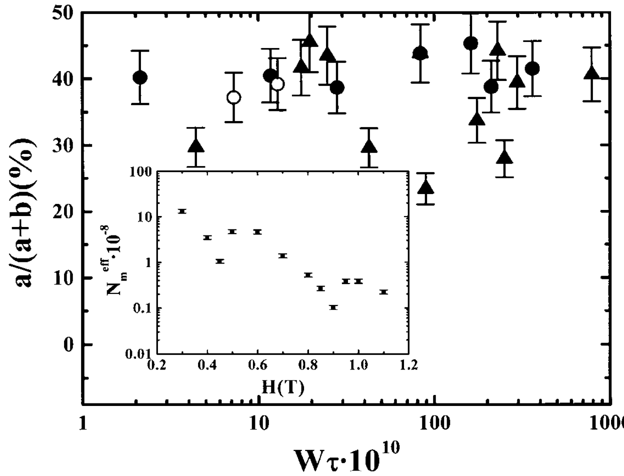

FIG. 4. Fractional echo height $a/(a + b)$ vs $W\tau$: (●) at $H = 0.45$ T with temperature as implicit parameter; (▲) at 2.4 K with magnetic field as implicit parameter. Open circle (○) data are taken with 30 μs delay between rf pulses while all other data are taken with 50 μs delay. Inset: Effective number of molecules affected by local field changes due to the magnetization flip of one molecule vs external magnetic field at 2.4 K.

T_2^{-1} (i.e., 4 kHz or 1 G in our case) in order to prevent the refocusing of the nuclear magnetization into the echo. Then for a reversal of the single Mn12 molecular magnetization one can estimate the range over which the dipolar field changes by 1 G. One finds $N_m^0 \approx 3 \times 10^4$. This number is much smaller than the saturated value of N_m^{eff} ($\cong 1/W\tau$), 10^7–10^{10}, which is deduced from experimental results (see the inset in Fig. 1). However, if the reversal of the magnetization occurs via a series of thermal fluctuations between intermediate levels with $\Delta m = \pm 1$ then the estimate of N_m^0 is much higher, namely, in the range 10^{12}–10^{16} depending on T and H values. Thus, in principle, the experimental determination of N_m^0 should distinguish if the reversal of the magnetization occurs via thermal steps or by quantum tunneling since in the former case the value of N_m^{eff} should be bigger. Unfortunately, since we are in the saturation regime the dips observed in the N_m^{eff} vs field (inset in Fig. 4) at the level crossing values, 0.45 and 0.9 T, do not contain information about the mechanism of reversal of the magnetization. In order to be in the nonsaturation regime (where the fractional echo change in Fig. 4 should be a linear function of $W\tau$) one should have $W\tau < 1$ implying $W\tau N_m^{\text{eff}} < 10^{-11}$–$10^{-12}$. This is barely achievable at temperatures below 1 K where W becomes of the order of 10^{-7}–10^{-8} sec^{-1} [6] (with $\tau = 50$ μsec).

In conclusion, we have shown that the NMR echo intensity in Mn12 is a function of time during the process of evolution of the total magnetization towards equilibrium. We have analyzed the phenomenon with the aid of a simple model and we have established that the experimental measurement of the echo vs time allows a direct measure of the relaxation rate of the magnetization with the possibility of discriminating in principle between thermal excitations over the barrier and tunneling transitions.

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